STATE OF OHIO
John J. Gilligan, Governor
DEPARTMENT OF NATURAL RESOURCES
William B. Nye, Director
DIVISION OF GEOLOGICAL SURVEY
Horace R. Collins, Chief

Report of Investigations No. 89

POTENTIAL USE OF BENEFICIATED OHIO CLAY IN THE RUBBER INDUSTRY

by

Richard W. Carlton

Columbus
1973

DEPARTMENT OF NATURAL RESOURCES

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ABSTRACT

The rubber industry in Ohio uses large quantities of kaolin each year. However, although Ohio has extensive deposits of clay relatively rich in kaolinite, none of it is used by the industry.

The grit content, particle-size distribution, moisture content, pH, brightness, and mineralogy of 14 water-fractionated clays from Ohio were determined. Chemical analyses of the 7 brightest Ohio clays were obtained and a modest amount of data determined on test specimens made from 2 Ohio clays whose physical properties approached rubber-grade clay standards.

All of the beneficiated Ohio clays have acceptable grit contents and particle-size distributions, but all are below rubber-grade clay standards in brightness and moisture. Of the tested Ohio clays, washed samples of the Sciotoville, Middle Kittanning, Lower Kittanning, and Clarion clays have the highest kaolinite-to-illite ratios and have the highest reflectance values.

The Sciotoville clay, although it is the brightest and has the highest kaolinite-to-illite ratio (17:1) of the tested Ohio clays, disaggregates with difficulty and thus is difficult to water fractionate. The Middle Kittanning, Lower Kittanning, and Clarion clays have kaolinite-to-illite ratios ranging from 2:1 to 4:1 and all have relatively high brightness values. They disaggregate readily and are easily water fractionated, yielding a low-grit clay with 72 to 81 percent of the clay particles less than 2μ in diameter.

The Harlem and Oak Hill clays have kaolinite-to-illite ratios of approximately 1:1, yet have high brightness values comparable to those of the Lower Kittanning and Middle Kittanning clays. The Harlem clay contains a variety of phyllosilicates in addition to dolomite, calcite, and quartz and is less likely to perform well in rubber-compounding tests.

The Meigs Creek clay, Bedford shale, Minford silt, and Wisconsinan clayey silt have low brightness values, low kaolinite-to-illite ratios, and a variety of phyllosilicates. The Meigs Creek shale, although it has a 3:1 kaolinite-to-illite ratio, has a very low brightness value.

Samples of the Sciotoville and the Lower Kittanning clays were chosen for rubber-compounding tests. The data from the rubber test specimens seem to suggest that, except for their color, at least some of the water-fractionated Ohio clays should perform about as well as kaolins in rubber products.

INTRODUCTION

The rubber industry in Ohio utilizes large quantities of clay. However, although Ohio is one of the leading producers of clay in the United States, no local clay is used for rubber manufacture.

Rubber-grade clays are mined in the United States almost exclusively in Georgia and South Carolina, where beds of almost-pure kaolin exist. In contrast clays mined in Ohio are underclays or lacustrine clays which in their crude form do not meet specifications for rubber-compounding clays.

Ohio clay production in 1971 was 2,252,748 short tons mined from 25 of the 88 counties in the state. Fire clay reserves for Ohio are estimated at 4,150 million tons (Cooper, 1970). If clay-processing technology advances as expected in the next 30 years, clay producers should be able to convert lower quality clays similar to those found in Ohio to raw material for paper coater, paint, rubber filler, and high-quality ceramics (Cooper, 1970).

The purpose of this investigation was to determine if Ohio's clays can be beneficiated so that they meet the standards of rubber-grade clays and, if so, how they compare in performance with commercially available rubber clays in actual rubber-compounding tests. The use of Ohio clays on a large scale by the rubber industry would eliminate the cost of transporting clays from other states and would establish a new market for clay producers in Ohio.

ACKNOWLEDGMENTS

This writer wishes to acknowledge Rubbermaid, Inc., for performing rubber-compounding tests and particularly Mr. Clayton Whipple of Rubbermaid for his assistance and critical reading of the manuscript. Appreciation is also extended to Harwick, Inc., for providing several of the commercial kaolins used in this investigation.

PHYSICAL PROPERTIES OF RUBBER-GRADE CLAYS

Rubber-grade clays are composed of very fine-grained well-crystallized kaolinite and are characterized by whiteness, high chemical and mineralogical purity, low moisture absorption, and low grit content.

Particle size is an important property of rubber-grade clays. Most such clays have at least 60 percent of the particles less than 2μ in diameter and have less than 0.4 percent grit greater than 44μ in diameter.

The grit content of rubber clays must be low because excessive amounts have deleterious effects on the physical properties of rubber, dull the knives of trimming machines, and cause wear of dies and rubber-mixing equipment (Anonymous, 1955).

The kaolins listed in "Materials and Compounding Ingredients for Rubber" (Del Gatto, 1970) illustrate the grain sizes desirable for rubber clays. Of 97 kaolins listed, 36 have data pertaining to the average grain size and 36 to the percent of particles less than 2μ in diameter (fig. 1).

Brightness is an extremely important physical property of rubber-grade clays. Reflectance value, measured on a G.E. brightness meter, should be greater than 70 percent; high-grade rubber clays generally have values ranging from 80 to 89 percent. Kaolins with low reflectance values discolor light-colored rubber stock.

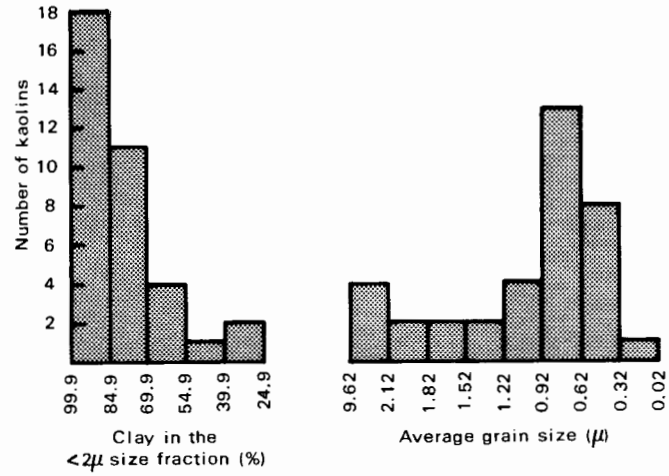

FIGURE 1.—Percentages of clay in the <2μ size fraction and average grain size of 72 commercial kaolins (Del Gatto, 1970).

Moisture content of rubber-grade clays is low, the upper limit being about 1 percent when the clay is dried at 105°C.

The pH values obtained from clay-water suspensions of commercial rubber clays are largely dependent on the processing steps involved. Thus pH values are usually included in the specification of rubber-grade clays in order to insure compatability between the clay and the remaining rubber-compounding ingredients. Of 53 rubber clays for which pH values were listed in Del Gatto (1970) 89 percent have a pH in the range 4½ to 7½.

SAMPLE LOCATIONS AND DESCRIPTIONS

The samples tested in this study were 14 clays and shales from Ohio (table 1, fig. 2) and 3 commercially

TABLE 1.—*Sample descriptions and locations*

Stratigraphic name	Sample number	Lithology	County	Township	Remarks
Middle Kittanning[1]	10-0484	Clay	Carroll	Brown	Underclay
Lower Kittanning[1]	10-0485	Clay	Carroll	Brown	Underclay
Lower Kittanning[1]	15-0235	Clay	Columbiana	Liverpool	Underclay, deep-mined
Bedford[2]	21-0885A	Shale	Delaware	Genoa	Red and gray
Clarion[1]	27-0023	Clay	Gallia	Greenfield	Underclay
Oak Hill[1]	40-0314	Clay	Jackson	Bloomfield	Underclay
Minford[3]	40-0926B	Clay	Jackson	Madison	Glacial lake clay, air-floated
Bedford[2]	51-0966B	Shale	Marion	Tully	Gray only
Meigs Creek[1]	61-0628	Shale	Noble	Jefferson	
Meigs Creek[1]	61-0632	Clay	Noble	Sharon	Underclay
Harlem[1]	61-0652	Clay	Noble	Olive	Underclay
Sciotoville[1]	73-0016	Flint clay	Scioto	Bloom	Underclay
Minford[3]	73-0970	Clay	Scioto	Madison	Glacial lake clay
Wisconsinan[3]	84-0627	Clayey silt	Washington	Lawrence	Lake silt

[1]Pennsylvanian [2]Mississippian [3]Pleistocene

prepared rubber-grade kaolins (RC-1, RC-2, and RC-3). The Ohio samples, 1 flint clay (Sciotoville, 73-0016), 7 plastic underclays (Middle Kittanning, 10-0484; Lower Kittanning, 10-0485, 15-0235; Clarion, 27-0023; Oak Hill, 40-0314; Meigs Creek, 61-0632; Harlem, 61-0652), 3 shales (Bedford, 21-0885A, 51-0966B; Meigs Creek, 61-0628), and 3 Pleistocene glacial lake clays (Minford, 40-0926B, 73-0970; Wisconsinan, 84-0627), were collected from central, southern, and eastern portions of the state.

A few samples which obviously would not meet rubber-clay standards were included for comparison,

FIGURE 2.–Sample location map.

but for the most part clays judged most likely to approach rubber-grade quality were chosen for the tests. One commercially prepared (air-floated) Ohio clay sample was tested; the other Ohio samples had received no prior processing.

FRACTIONATION AND TESTING PROCEDURES

General statement

Rubber-grade clays are produced either by air-flotation or water-fractionation techniques. Air flotation is the simpler and cheaper method, but requires high-purity high-brightness crude clays. Most of the clays used by the rubber industry are of this type. Water fractionation, although a more involved process than air flotation, enables the producer to control particle size, to bleach the clay, to surface treat the clay, and to adjust the pH if desirable. Water fractionation is thus necessary for clays in which the brightness, particle-size distribution, or grit content fails to meet rubber-clay standards.

Method of fractionation

The crude clay was first crushed to granule size (<4 mm) and a 2,000-g split was soaked for 18 hours or more in 2 liters of tap water and 100 ml of 0.5N sodium metaphosphate. After soaking, the slurry was mixed in a Waring Blendor for 1 minute, then placed in a large plastic container and diluted with tap water to make 34 liters of suspension. The clays were dispersed with 26 to 52 g of sodium metaphosphate.

In the water-fractionation process the particle size of the clay can be controlled simply either by selecting different settling intervals at which to withdraw the desired size fraction or by varying the depth at which the suspension is drawn off. Calculations based on the particle-size distribution of the crude clay show that by making use of only the <4μ size fraction of each clay[1], the quantity of particles less than 2μ in diameter is increased to 60 to 70 percent in the washed clay (table 4).

A 36-liter sample of the required size fraction was obtained by thoroughly mixing the clay suspension, waiting 2 hours, then siphoning the <4μ size fraction at the 10-cm depth. This procedure was repeated four times or until insufficient suspension was left for additional siphonings, then 7 liters of water were added and a fifth and last siphoning performed.

Two methods were used to obtain the dried fractionated clay. First and most simply, the suspension was evaporated directly. This method does not eliminate the original soluble salts in the clay or the dispersant previously added to the clay suspension.

In the second method the clay suspension was flocculated with sodium chloride and the supernatant drawn off and discarded. The flocculated clay was then poured into cellulose dialyzing tubing, sealed, and placed in slowly circulating tap water for 2 to 3 days. At the end of this time most of the sodium chloride and an unknown amount of dispersant were eliminated from the clay. Samples processed in both ways were dried at 105° to 110°C, then pulverized to a fine powder.

Particle size

Grit content (>44μ) was determined in both the crude and washed samples. In each case 100 g of sample was soaked overnight in about 400 ml of distilled water with a small amount of dispersant added. The clay slurry was mixed in a Waring Blendor for 5 minutes and then the slurry was wet sieved through a 325-mesh screen. Tap water was used to wash the more reluctant particles through the screen. The residue caught on the screen was transferred to a watch glass of known weight and dried at 110°C.

On the crude clay samples the amounts of material less than 44, 10, 5, 4, 3, 2, 1, and ½μ were determined; on the water-washed clays the amounts of sample less than 44, 5, and 2μ were measured. Procedures outlined by Folk (1965) for pipette analysis of clays were followed.

Moisture content

Moisture loss of the air-dry samples was determined after heating them to 105°C.

pH

A 100-g sample of the water-fractionated powdered clay was mixed with 250 ml of distilled water for 5 minutes in a Waring Blendor. The pH of the distilled water used was 5.80±0.05. Temperature of the slurry was adjusted to 25°C, and the pH meter was standardized with buffer tablets at pH 7 and pH 4. Readings were taken during stirring and after the needle of the pH meter had stabilized.

Brightness

Tests of brightness are generally performed using a reflectometer designed to measure the reflectance of a filtered light directed perpendicular to or at some known angle to the sample.

A reflectometer was not available for this study, but a means of determining the relative brightness of the clays was devised by using a Leitz Ortholux microscope and photometer setup for reflectance microscopy. The tests were conducted using a 10X eyepiece

[1]In the two Minford samples the original particle-size distribution approximated that of rubber-grade clay, and the <44μ size fraction was used.

and an objective with a magnification number of 5.6 and a numerical aperture of 0.15P in conjunction with a model 520-M photometer manufactured by Photovolt Corporation. Green light (5400Å) was used for illumination. An MgO powder was used as a standard and was arbitrarily assigned a reflectance of 90 percent. The brightness values of three rubber-grade clays were used for comparative purposes. Reflectance values of the MgO standard were determined prior to and after measurement of each unknown.

The clay samples were prepared for reflectance determinations by packing the clay into a 1-inch ID Buehler mold assembly. A smooth clay surface was obtained by applying 55 to 60 psi pressure to the mold.

The prepared clay sample was placed in a small lightproof chamber that could be attached snugly to the objective of the microscope. Although microscope accessory openings and miscellaneous light leaks in the microscope rendered the system somewhat less than completely lightproof, the extraneous light was not intense enough to register on the least sensitive scale setting of the photometer.

X-ray analyses

The Ohio samples were x-rayed for the purpose of determining the clay minerals. The $<4\mu$ ($<44\mu$ in the case of the Minford samples) size fraction of each clay was pipetted onto a glass slide and air dried. One subsample of each clay was glycolated in an airtight container for at least 24 hours before being x-rayed; another subsample was x-rayed in the untreated state. Glycolated samples suspected of containing chlorite were heated for 2 hours at 500°C and x-rayed a second time.

X-ray patterns were run on a Norelco x-ray diffractometer using Ni-filtered CuKα radiation at 35 kv and 20 ma.

Because chlorite and montmorillonite were relatively minor constituents of the clays tested, the 7Å peak in these patterns generally represented kaolinite rather than chlorite, and the broad peaks on the low-angle side of illite generally represented mixed-layer clays rather than montmorillonite or chlorite. Ratios of peak areas of kaolinite (and chlorite) to illite (and mixed-layer clays) were determined so that a rough estimate of the proportion of kaolinite (and chlorite) to illite (and mixed-layer clays) in each sample could be made.

Chemical analyses

The chemical analyses of the clays were performed on a Perkin-Elmer model 303 atomic absorption spectrophotometer. Weighed portions of the 950°C ignition-loss residue were dissolved in 40 percent hydrofluoric acid in a Parr 25 ml Teflon-lined acid-digestion bomb at 140°C; dry addition of boric acid and nitric acid followed. The dissolution technique is similar to that described by Langmyhr and Paus (1968).

RESULTS AND DISCUSSION

Residue

The residue (mineral grains and clay aggregates) in the crude clay was determined so that the relative amount of the clay sample easily disaggregated and recovered could be determined (table 2). The fractionated clays must be nearly free of grit (not more than 0.4 percent greater than 44μ) in order to meet

TABLE 2.—*Residue left on 325-mesh screen*

Stratigraphic name	Sample number	Crude clay mixed 5 minutes in Waring Blendor		Water-fractionated clay mixed 5 minutes in Waring Blendor
		Residue (% of sample)	Aggregates (% of residue)	Residue (% of sample)
Minford	73-0970	0.30	0.0	0.28
Minford[1]	40-0962B	0.83	80.0	
Bedford	51-0966B	3.10	46.0	0.04
Clarion	27-0023	3.50	14.0	0.02-
Bedford	21-0885A	4.60	?	0.02
Middle Kittanning	10-0484	7.10	41.0	0.15
Oak Hill	40-0314	15.10	22.0	0.73
Lower Kittanning	15-0235	16.80	67.0	0.28
Lower Kittanning	10-0485	17.60	15.0	0.48
Harlem	61-0652	18.00	90.0	0.83
Meigs Creek	61-0628	20.20	40.0	0.07
Meigs Creek	61-0632	22.20	47.0	0.05
Wisconsinan	84-0627	22.50	0.0	
Sciotoville	73-0016	67.00	98.0	0.76

[1]Commercially prepared air-floated clay.

TABLE 3.—*Residues of 13 washed Ohio clays compared with residues of 47 rubber-grade clays*

Rubber-grade clays		Water-fractionated Ohio clays	
Number	Range of residue (%)	Number	Range of residue (%)
2	0.5 -1.0	4	0.5 -1.0
28	0.2 -0.4	4	0.2 -0.4
17	0.01-0.1	5	0.01-0.1

rubber clay specifications.

The data in table 2 suggest that the Sciotoville clay is not suited for water fractionation because a large amount of the clay is not readily disaggregated. The Wisconsinan, Meigs Creek, Lower Kittanning, and Oak Hill samples contain residues composed of large amounts of mineral grains, which decrease the recoverable portion of the crude clay. In each of the other samples, although residue may be high, a significant amount of the >44μ fraction (325 mesh) is composed of aggregates which can be recycled.

The residue percentages for the water-fractionated samples are within the limits for rubber-grade clays. Table 3 compares the residue data for the washed Ohio samples with those (Del Gatto, 1970) for 47 commercially available rubber clays.

Particle size

Particle size is an important property of rubber-grade clays. Normally most such clays have at least 60 percent of the particles less than 2μ in diameter. Table 4 lists the particle-size distributions determined in this study for both crude and water-fractionated clays.

In the crude state most of the clays tested have poor or unacceptable particle-size distributions for rubber compounding. The Minford silt appears to be the only good rubber-grade clay in this respect. However, after water fractionation, all of the clays tested possessed acceptable, although not extremely good, particle-size distributions for rubber-grade clays.

Moisture content

Moisture determinations were performed on the rubber clays RC-1, RC-2, and RC-3 and on the 14 water-washed Ohio clays. The data (table 5) indicate that the Ohio clays, after being allowed to equilibrate with room humidity, are more hygroscopic than the three commercial rubber-grade clays. If the Ohio clays are properly sealed and not allowed direct access to the air after drying, however, the moisture content should remain near 1 percent from the time the clay is dried to the time it is used in rubber compounding.

pH

The pH of a rubber-clay suspension can be altered by bleaching, by the addition of dispersant, or by the addition of weak acid for flocculation. Table 6 lists the pH values of the water-fractionated clays.

Brightness

Three separate brightness determinations were made on each clay; average values are shown in table 7. These data, however, represent only the relative order of brightness of the 17 samples included in this

TABLE 4.—*Particle-size distribution of crude and water-fractionated clays*

Stratigraphic name	Sample number	Crude clay (%)									Water-fractionated clay (%)	
		<44μ size fraction								<2μ size fraction		
		44-10μ	10-5μ	5-4μ	4-3μ	3-2μ	2-1μ	1-0.5μ	<0.5μ		<5μ	<2μ
	RC-1										99.2	97.3
Minford	73-0970	3.5	3.5	3.1	4.5	7.3	14.9	14.9	48.4	78.2	93[1]	77[1]
Minford	40-0926B	1.3	2.3	6.0	5.0	9.0	15.4	15.4	46.5	77.3	93[1]	76[1]
Middle Kittanning	10-0484	9.8	9.8	9.8	7.1	9.4	9.4	18.5	26.3	54.2	98	81
Wisconsinan	84-0627	28.8	12.2	3.2	4.0	5.4	7.9	6.5	32.0	46.4	98	83
Oak Hill	40-0314	12.6	15.2	5.9	8.5	11.5	15.6	11.1	19.6	46.3	94	75
Sciotoville	73-0016	30.9	8.8	6.6	3.7	5.1	10.3	8.8	25.7	44.8	95	83
Clarion	27-0023	15.0	13.0	13.0	9.2	10.6	14.7	9.6	15.0	39.3	97	73
Lower Kittanning	10-0485	27.1	16.0	5.2	6.9	8.3	12.8	8.3	15.3	36.4	95	74
Bedford	21-0885A	16.5	14.4	14.4	9.1	10.9	13.3	8.1	13.3	34.7	96	68
Bedford	51-0966B	20.2	19.8	6.8	8.4	9.1	12.5	8.7	14.4	35.6	97	72
Harlem	61-0652	24.6	19.7	5.9	9.4	9.9	12.8	5.9	11.8	30.5	96	64
Lower Kittanning	15-0235	24.6	23.8	7.1	7.5	8.3	10.7	7.1	10.7	28.5	96	72
Meigs Creek	61-0632	28.0	21.8	6.7	7.1	8.4	10.7	4.9	12.4	28.0	95	63
Meigs Creek	61-0628	38.1	20.0	5.6	6.1	7.4	7.4	4.7	10.7	22.8	96	70

[1]Minford samples were water fractionated in such a manner that the <44μ size fraction was recovered.

TABLE 5.—*Moisture content of 3 commercial rubber-grade clays and 14 fractionated and pulverized Ohio clays*

Stratigraphic name	Sample number	Moisture content (%)
	RC-1	0.67
	RC-2	0.38
	RC-3	1.22
Middle Kittanning	10-0484	2.19
Lower Kittanning	10-0485	2.15
Lower Kittanning	15-0235	1.90
Bedford	21-0885A	1.65
Clarion	27-0023	1.75
Oak Hill	40-0314	2.13
Minford	40-0926B	1.52
Bedford	51-0966B	1.70
Meigs Creek	61-0628	not determined
Meigs Creek	61-0632	2.59
Harlem	61-0652	2.82
Sciotoville	73-0016	2.18
Minford	73-0970	2.00
Wisconsinan	84-0627	1.64

report and should not be compared with brightness values commonly cited in the literature.

Table 7 indicates that the three commercial kaolins, RC-1, RC-2, and RC-3, are significantly brighter than the brightest water-washed Ohio clay. In the interest of possible future use, however, the seven brightest Ohio samples were chosen for additional testing and for chemical analyses.

Because the Sciotoville is highly resistant to disaggregation but possesses the highest brightness value for the Ohio clays, tests were performed to determine whether dry grinding prior to water fractionation would decrease brightness. A test performed on the Sciotoville, but not shown in table 7, indicates that pulverization prior to water fractionation increases the amount of recoverable clay without noticeably decreasing the brightness.

Thus Sciotoville clay, which is not disaggregated in the first fractionation cycle, could conceivably be repulverized until a significant portion of the clay is fine enough for rubber standards.

TABLE 6.—*Values of pH for the water-fractionated clays*[1]

Stratigraphic name	Sample number	pH
Bedford	21-0885A	7.65
Minford	40-0926B	7.55
Bedford	51-0966B	7.35
Meigs Creek	61-0632	7.30
Clarion	27-0023	7.05
Wisconsinan	84-0627	7.05
Minford	73-0970	6.75
Harlem	61-0652	6.50
Oak Hill	40-0314	6.10
Middle Kittanning	10-0484	6.05
Lower Kittanning	15-0235	5.95
Sciotoville	73-0016	5.87
Meigs Creek	61-0628	5.65
Lower Kittanning	10-0485	5.20

[1]The pH of the distilled water used in making the slurry was 5.80±0.05.

X-ray analyses

Table 8 summarizes the mineralogical data obtained from the x-ray analyses of the clays. Samples RC-1, RC-2, and RC-3 are nearly pure kaolins. The water-fractionated Ohio clays, with the exception of the Sciotoville clay, contain a wide variety of clay minerals and quartz; a few contain carbonate minerals. Illite ranks second to kaolinite as the most abundant mineral in most of these samples.

Mica is reported to collect on the inner surface of dies during certain rubber-manufacturing processes (Anonymous, 1955). However, mica apparently is not deleterious to rubber itself because ground muscovite is used in some instances as a filler in rubber (Del Gatto, 1970). According to Grim (1962) the only apparent reason clays other than pure kaolin are not used is because of the lower brightness and variable chemical composition of most clays and shales; it appears likely that the mineralogy *per se* is not an important factor in determining whether a clay is

TABLE 7.—*Relative brightness of 14 Ohio clays and 3 rubber-grade kaolins*

Stratigraphic name	Sample number	Relative brightness (%)
	MgO standard	90
	RC-1	83
	RC-2	82
	RC-3	78
Sciotoville	73-0016	61
Harlem	61-0652	59
Lower Kittanning	10-0485	59
Lower Kittanning	15-0235	59
Oak Hill	40-0314	56
Middle Kittanning	10-0484	54
Clarion	27-0023	50
Meigs Creek	61-0632	49
Meigs Creek	61-0628	45
Bedford	51-0966B	45
Minford	73-0970	44
Bedford	21-0885A	<44
Minford	40-0926B	<44
Wisconsinan	84-0627	<44

TABLE 8.—*Mineralogy of the water-fractionated clays*

Stratigraphic name	Sample number	Kaolinite	Illite	Mixed-layer clays[1]	Chlorite	Montmorillonite	Quartz	Dolomite	Calcite	K:I[2]
Sciotoville	73-0016	x	x		x					17:1
Middle Kittanning	10-0484	x	x	x		x	x			4:1
Clarion	27-0023	x	x	x			x			3:1
Meigs Creek	61-0628	x	x	x	x		x			3:1
Lower Kittanning	15-0235	x	x	x			x			2:1
Lower Kittanning	10-0485	x	x	x			x			2:1
Oak Hill	40-0314	x	x	x			x			1:1
Harlem	61-0652	x	x	x	x	x	x	x	x	1:1
Meigs Creek	61-0632	x	x		x	x	x			1:1
Wisconsinan	84-0627	x	x	x			x			less than 1:1
Minford	73-0970	x	x		x		x	x	x	less than 1:1
Bedford	51-0966B	x	x	x	x		x			less than 1:1
Bedford	21-0885A	x	x	x			x			less than 1:1
Minford	40-0926B	x	x		x		x	x	x	less than 1:1

[1]Mostly clays of irregular illite-montmorillonite interstratification.
[2]Kaolinite (and chlorite) to illite (and mixed-layer clays) ratio.

suitable for rubber compounding.

Chemical analyses

Partial chemical analyses were performed on eight samples. Seven of the analyses were on water-washed clays and one was on the untreated Sciotoville clay. The crude Sciotoville clay was chemically analyzed to see if the unbeneficiated clay was suitable for dry grinding and air flotation rather than water-fractionation treatment.

The seven water-washed Ohio samples contain more Fe_2O_3 than is normally found in rubber-grade clays. However, only certain salts of iron are deleterious to rubber compounds, and only actual testing of the clay in rubber compounds can determine the effects, if any, that the iron may have on the rubber.

Except for the sample of Harlem clay, which contains considerable amounts of dolomite and calcite, the CaO content compares favorably with that found in rubber-grade clays; MgO and K_2O are slightly higher than in rubber kaolins because of the presence of illite, montmorillonite, chlorite, and mixed-layer clays.

The sodium content is dependent on the type of

TABLE 9.—*Chemical analyses of 7 water-fractionated clays and 1 crude clay from Ohio compared with the chemical analysis of a typical rubber-grade clay*

Stratigraphic name	Sample number	Oxide (%)									Ignition loss
		SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	TiO_2	MnO	Na_2O	K_2O	
Sciotoville[1]	73-0016	45.33	33.84	4.90	0.33	0.10	2.03	0.029	0.23	0.88	12.63
Sciotoville[2]	73-0016	39.64	37.62	1.94	0.63	0.62	1.58	0.007	2.84	0.94	13.27
Oak Hill[2]	40-0314	50.96	27.96	3.61	1.07	0.95	1.14	0.013	1.39	3.54	8.24
Harlem[2]	61-0652	37.38	18.20	4.54	3.88	12.84	0.59	0.143	2.08	2.91	16.58
Lower Kittanning[2]	15-0235	49.50	31.30	1.48	0.78	0.38	1.80	0.005	2.07	3.97	9.28
Lower Kittanning[3]	10-0485	52.99	29.77	2.48	0.97	0.34	1.31	0.007	0.18	3.87	7.92
Middle Kittanning[3]	10-0484	48.89	30.75	3.57	0.71	0.26	1.21	0.005	0.75	2.93	9.49
Clarion[3]	27-0023	52.75	30.76	1.86	0.78	0.47	1.36	0.00	0.18	2.97	9.02
Commercial rubber clay[4]		45.42	38.79	0.31		0.35	1.59		0.13	0.02	13.79

[1]Crude clay.
[2]Water fractionated and evaporated.
[3]Water fractionated and dialyzed.
[4]Typical chemical analysis of Champion clay, produced by National Kaolin Products Co. (courtesy of Harwick, Inc., Akron, Ohio).

TABLE 10.—*Results of physical tests on 4 rubber test specimens*

Stratigraphic name	Sample number	Modulus (300%)	Ultimate tensile strength (psi)	Elongation (%)	Tear (ppi)	Hardness (Shore A)
	Rubber-grade clay A[1]	602	917	433	109	65
	Rubber-grade clay B[2]	673	856	392	106	68
Lower Kittanning	10-0485	511	881	508	121	63
Sciotoville	73-0016	861	932	350	127	68

[1]McNamee clay (kaolin) produced by R. T. Vanderbilt Co., Inc., and used as a control clay in this series of tests.
[2]Harwick #62 clay (kaolin) produced by Harwick, Inc., and used for comparison with the Ohio clay samples.

treatment the sample underwent. The crude Sciotoville clay reflects the amount of sodium occurring naturally in the clay. Beneficiated Sciotoville clay, Harlem clay, Lower Kittanning clay (15-0235), and Oak Hill clay reflect for the most part the amount of sodium metaphosphate added as dispersant. Beneficiated Clarion clay, Middle Kittanning clay, and Lower Kittanning clay (10-0485) were treated with sodium metaphosphate and NaCl as dispersant and flocculant, respectively, but contain less sodium because of dialysis treatment after flocculation. The manganese content of all the clays is negligible.

The results of the chemical analyses are shown in table 9.

Rubber-compounding tests

Generally it is difficult to predict the behavior of

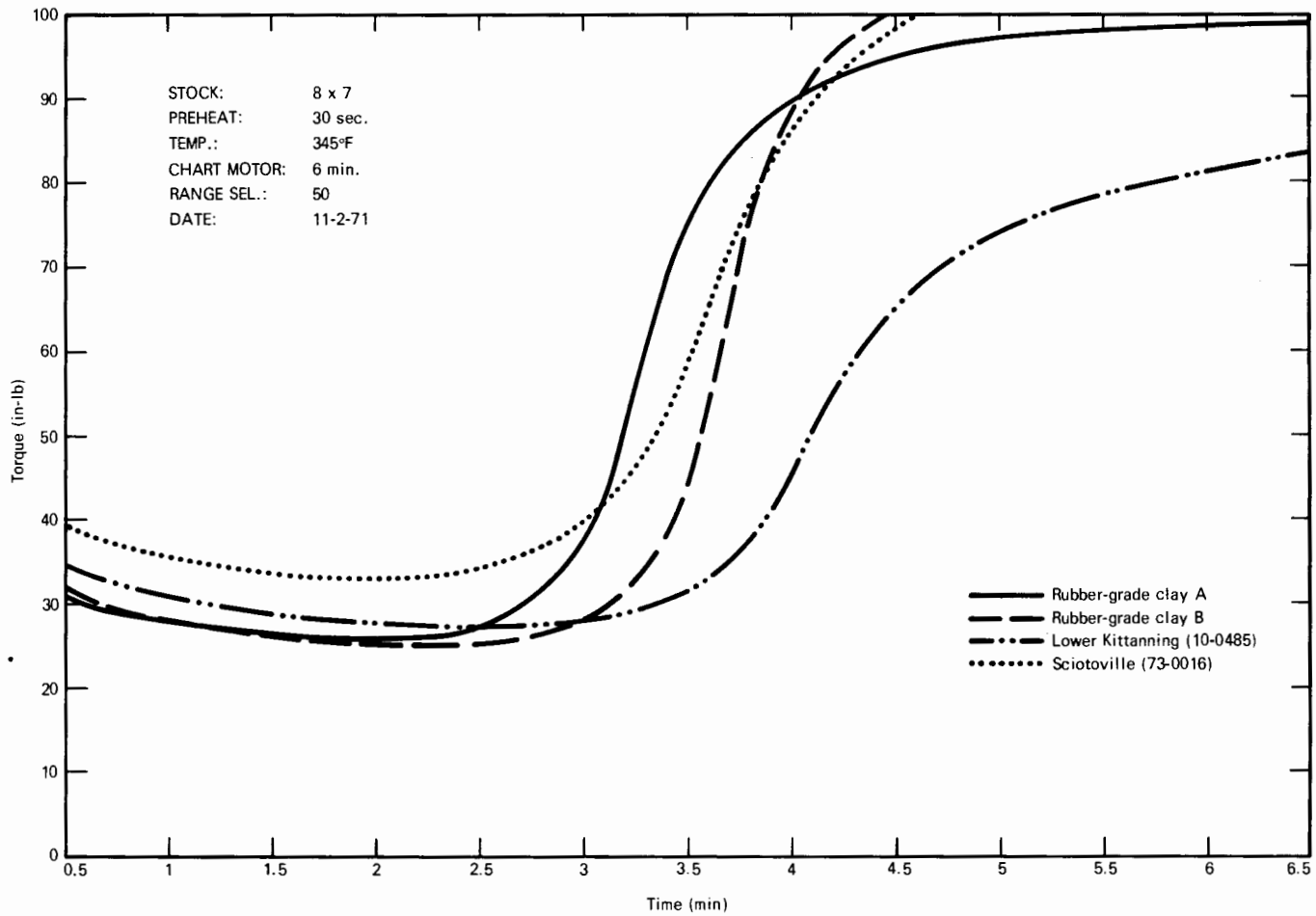

FIGURE 3.—Cure curves.

a clay in rubber products without performing actual rubber-compounding studies. In order to obtain some idea of how two Ohio clays from the study suite would behave in rubber products, an Ohio rubber company agreed to perform a modest number of tests. The results are shown in table 10 and figure 3.

In table 10 "Modulus 300%" indicates the tension stress in lbs/in^2 required to stretch the rubber specimen by 300 percent. The percent elongation indicates the amount of stretching that can take place before rupture occurs, and tear indicates the load required to extend a tear or cut of standard depth in the specimen. Hardness measures the resistance to indentation and is an expression of the elastic modulus. Hardness tests were performed on a type Shore A durometer.

Figure 3 shows the results obtained from a Monsanto rheometer. The data indicate that (1) the initial viscosities of the two rubber-grade clay compounds are slightly lower than the viscosities of the Ohio clay-rubber mixtures, (2) the cure rates of the Sciotoville clay and of the Lower Kittanning clay are lower than the rates for the rubber-clay compounds, (3) the Sciotoville clay has the highest shear modulus of the four tested clays, (4) the shear modulus of the Lower Kittanning clay is still increasing after 6 minutes of cure time, but this sample has apparently the lowest value of the four test specimens, and (5) the time required to attain optimum cure is longer for the Lower Kittanning clay than for the other three test specimens.

Except for the clay, the ingredients used in compounding each of the four rubber test specimens were identical. Thus it cannot be assumed that the results in figure 3 and table 10 reflect the most suitable ingredients or conditions possible for obtaining the highest quality rubber with a particular clay. On the other hand, the tests which were performed suggest that at least some of the washed Ohio clay should perform about as well as kaolins presently used in rubber products.

The physical characteristic which presents the greatest obstacle to the use of Ohio clays in rubber is low brightness value.

SUMMARY AND CONCLUSIONS

Results of this study are summarized in table 11. Of the tested Ohio clays the Sciotoville clay, although it slakes poorly, has the highest kaolinite-to-illite ratio and is the brightest. It contains no quartz detectable by x-ray diffraction analyses and only minor amounts of illite and chlorite. Of the 14 Ohio samples tested, this clay comes closest to rubber-grade clay standards.

The most serious disadvantage of the Sciotoville clay is its resistance to disaggregation. Air flotation of the clay would be the most practical method of processing if brightness were not a factor. Water fractionation not only greatly increases the brightness, but eliminates 60 percent of the iron (see chemical analyses, table 9) found in the untreated Sciotoville clay.

Pulverizing prior to water fractionation increases the amount of recoverable Sciotoville clay without noticeably decreasing the brightness. The Middle Kittanning clay, the Lower Kittanning clays, and the Clarion clay are similar in having kaolinite-to-illite ratios ranging from 2:1 to 4:1, and all have relatively high brightness values. They disaggregate readily and are easily water fractionated, yielding a low-grit clay with 72 to 81 percent of the clay particles less than 2μ in diameter.

TABLE 11.—*Summary of test results*

General suitability for rubber manufacture	Stratigraphic name	Sample number	Remarks
Group A. Requires least amount of beneficiation to meet or approach rubber-grade clay standards	Sciotoville	73-0016	Brightest of the test samples, highest kaolinite/illite ratio, overall suitability good
	Middle Kittanning	10-0484	Fair brightness, overall suitability good
	Lower Kittanning	10-0485	Fair brightness, overall suitability good
	Lower Kittanning	15-0235	Fair brightness, overall suitability good
Group B. Requires moderate amount of beneficiation to meet or approach rubber-grade clay standards	Oak Hill	40-0314	Fair brightness, overall suitability fair
	Clarion	27-0023	Poor brightness, overall suitability fair
Group C. Requires maximum amount of beneficiation to meet or approach rubber-grade clay standards	Harlem	61-0652	Fair brightness, high in carbonate minerals, overall suitability poor
	Bedford	21-0885A	Poor brightness, overall suitability poor
	Minford	40-0926B	Poor brightness, overall suitability poor
	Bedford	51-0966B	Poor brightness, overall suitability poor
	Meigs Creek	61-0628	Poor brightness, overall suitability poor
	Meigs Creek	61-0632	Poor brightness, overall suitability poor
	Minford	73-0970	Poor brightness, overall suitability poor
	Wisconsinan	84-0627	Poor brightness, overall suitability poor

The Harlem clay and Oak Hill clay have kaolinite-to-illite ratios of approximately 1:1, yet have high brightness values compared to the other clays tested. The Harlem clay contains a variety of phyllosilicates in addition to dolomite, calcite, and quartz. The amount of clay particles less than 2μ in size is from 8 to 17 percent lower than in the four underclays described above, and this clay is probably less likely to perform well in rubber-compounding tests. The Oak Hill clay, because of its lower kaolinite-to-illite ratio, is probably less suitable for rubber compounding than the Lower Kittanning, the Middle Kittanning, and the Clarion clays.

The two water-fractionated clays used in the rubber-compounding tests are inferior in color and contain more water than is permissible in rubber-grade clays. Whiteness of Ohio clays can probably be enhanced slightly by bleaching, although even with extreme bleaching these clays will probably not compare in whiteness to pure kaolins. Moisture adsorption can probably be kept to a minimum by shipping the clay in airtight tank cars or bags.

Because large quantities of clay are utilized in rubber products, any clay considered for such use must have relatively uniform chemical composition and considerable reserves. At least a few of Ohio's underclays, after beneficiation by water fractionation, should meet all but the color specification of rubber-grade clays. Some beneficiated Ohio underclays probably could be used in dark or black rubber products now; however, as long as high-grade kaolins are available, the cost for the research and development necessary before a clay can be used in rubber manufacturing is prohibitive.

Ohio clays will become more competitive with kaolins as additional advances in bleaching and clay-mineral separation techniques are made.

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